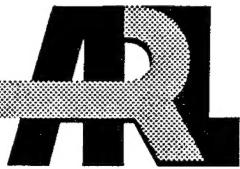


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A METHOD FOR SIMULTANEOUSLY ENHANCING THE TRANSITION
TEMPERATURE AND INCREASING MECHANICAL STRENGTH
OF YTTRIUM BARIUM COPPER OXIDE ($\text{YBa}_2\text{Cu}_4\text{O}_8$)

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TEMPERATURE AND INCREASING MECHANICAL STRENGTH OF
YTTRIUM BARIUM COPPER OXIDE ($\text{YBa}_2\text{Cu}_4\text{O}_8$)

INTRODUCTION

In December 1986 High Temperature Superconductors (HTSs) were discovered.¹ These materials promise to provide thin film electronic circuit components with higher speed, smaller size, increased sensitivity and reduced noise. One of the most popular HTS materials is $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y123) which shows a transition temperature (T_c) of 89.5 to 91K.²

Unfortunately, Y123 has some disadvantages that limit its technological usefulness. For example, its microwave applications are limited by a phase transition at 700C at which twinning and stress arise that increase the resistivity of the film's surface. Y123 also loses O_2 at temperatures above 400C resulting in reduction of T_c and a broadening of the transition. This is especially troublesome in the fabrication of multiple layer devices because deposition of successive layers requires heating which degrades the underlying layers by causing O_2 loss.

$\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y124) was found to have a slightly lower range of T_c from 82-90K³, but to be free from deleterious characteristics in the temperature range used for most device fabrication (500-825C). Y124 can be heated to 850C without serious O_2 loss. It was also found that further improvements are attainable through chemical substitutions at 760 Torr of O_2 and higher pressures.^{4 5 6 7 8} The substitutions are Ca for Y to raise the T_c and Li for Cu to enhance sintering. In this report we describe the preparation of Y124 and (Y124 with substitutions of Ca and Li).

SAMPLE PREPARATION

PREPARATION AND PROPERTIES OF POLYCRYSTALLINE Y124 AND $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$

Measurements of the critical temperature (T_c) were made by two methods; a microwave technique (referred to here as the RF technique) which measured the surface resistivity at 35 GHz, and an AC technique which measured the magnetic screening provided by the sample. For any sample, the transition temperature measured by the RF technique will be slightly different from the T_c determined by the AC technique for two main reasons. First, the thermocouple in the RF measurement is closer to the sample than is the temperature sensor in the AC system. Second, the RF technique measures only the electrical properties of the one surface that is facing the cavity, while in the AC method, the entire bulk of the sample contributes to the magnetic screening. Because of the differences in the two systems, the T_c and the transition width for any sample will depend upon the measurement technique used. For several samples discussed here, results from both the RF and the AC methods are reported.

Twelve samples of Y124 or $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ were prepared as summarized in Table 1. Polycrystalline specimens were prepared from two different precursors. One precursor was a gel prepared by dissolving stoichiometric amounts of nitrates of copper, barium, and yttrium in aqueous solution and the addition of Knox® gelatin to produce a gel. The gel was slowly dried at 38C in a vacuum oven. The second precursor was a mixture of CuO , BaCO_3 and Y_2O_3 . These oxides were weighed out in stoichiometric amounts and mixed by grinding together in a boron carbide mortar and pestle. Ca and lithium were added as CaCO_3 and Li_2CO_3 in stoichiometric amounts.

Table 1. Preparation and Results

Sample #	T_c by AC Susceptibility (K) (cool down)	T_c by RF Surface Resistivity (K) (cool down)	Manner of Preparation of Bulk	Sample Compound	Process (C)	Results
1			nitrates and gelatin; heated in O ₂ ; fired in O ₂	aim at Y124		superconducting but not Y124; XRD contained both Y123, Y124
2	77.9 (width 4.2)	77.4 (width 5.2)	fired in helium; 775-825C for 20 hours; nitrates and gelatin	aim at Y124	775-825C for 20 hours	Y124 partially achieved
3	78.4 (width 4.2)	63.8 (width 60.5)	nitrates and gelatin; fired in vacuum; 775-825C for 68 total hours; in O ₂	aim at Y124	ground powdered gel	tried to make Y124, made Y123; poor result; XRD gave Y123 with some Y124
4	61.5 (width 13)		powder mixed in mortar; sinter in vacuum 750C, 48 hours	aim at Y124	750C for 48 hours O ₂ flow; then 4 days at 800C	
5A	76.6 (width 6.8)		powder mixed in mortar	first successful attempt to produce Y124	800C for 96 hours with O ₂ flow	XRD gave Y124
5B	85.4 (width 4.1)		powder mixed in mortar		920C in O ₂ for 4 minutes; 750C for 1 minute; 450C for 2 hours in O ₂	XRD gave Y123 + CuO
6A		no resistivity RF resonance	powder mixed in mortar		825C for 100 hours with O ₂ flow	XRD gave Y124
6B		74.0 got resonance			825C for 100 hours with O ₂ flow	XRD gave Y124
6C	79.2 (width 7.2)	there was resonance	powder mixed in mortar		825C for 100 hours with O ₂ flow	XRD gave Y124
7	80		powder mixed in mortar		sinter at 825C for 100 hours	
8	73.5 (width 4.4)		powder mixed in mortar	Ca sub Z = .025	calcine 790C in vacuum; hold for 48 hours; down slowly to 100, sinter 825C for 100 hours in O ₂	

...Table 1 continued on following page.

Table 1. Preparation and Results (continued)

Sample #	T_c by AC Susceptibility (K) (cool down)	T_c by RF Surface Resistivity (K) (cool down)	Manner of Preparation of Bulk	Sample Compound	Process (C)	Results
9A	69.4 (width 3.1)		powder mixed in mortar; calcine at 770C in vacuum; (sinter 825C for 120 hours)	Ca sub Z = .05 Y.95 Ca .05 Ba2 Cu4 O8	(in Al2 O3 boat in quartz tube 800C in O2 for 48 hours; cooled to 300C in O2); made a thin film by pulsed laser ablation 150 mTorr O2; film was shiny but XRD gave Y123+Cu O	film had retreated from the edges and changed from Y124 to Y123 by laser action in O2 atmosphere
9B			Calcine 770 for 70 hours; sintered at 825 in O2 for 120 hours	Ca sub Z = .05 Y.95 Ca .05 Ba2 Cu4 O8	heat 920C for 1-4 minutes	Y123 +CuO by XRD
9C	75 (width 2)		powder mixed in mortar	Ca sub Z = .05 Y.95 Ca .05 Ba2 Cu4 O8	Calcine 775C vacuum for 60 hours; sinter 825C for 120 hours with O2	
10		lowest surface resistivity		Ca sub Z = .025		
11			powder mixed in mortar; axial press 3.45×10^7 Pa; isostatic 3.45×10^8 Pa	2 Ba F2 + $\frac{1}{2}$ Y2 O3 + 4 Cu O	800C in 6 hours; hold 12 hours; cool 10 hours	
12	68.9	59.8 (width 5.8)	powder mixed in mortar	Li sub X = .05	laser ablation 730C + pres 250 mTorr	XRD lattice constant contraction; XRD did not yield Y124; brown thin film; very large resistance; annealed at 800C for 2 hours in O2; XRD showed peaks of MgO and several small peaks which could be Y123 or Y124

Notes: Ca sub gives low surface resistance 120 m Ω at 34K and 35 GHz.

Width is the spread in the temperature reading.

Samples #1-3 were prepared from the nitrate precursors. The dried gel for these samples was ground to a powder, placed in an alumina crucible, and fired in either oxygen (sample #1), helium (sample #2), or vacuum (sample #3). In general, samples #1-3 contained both the Y123 and Y124 phases. Sample #2, which was fired at 775-825C for 20 hours, showed a T_c (RF) of 78.7K and a transition width of 6.6K. For the sample, the AC technique showed a T_c of 76.3K and a transition width of 3.4K. No T_c measurement of sample #3 was attempted because the X-ray Diffraction (XRD) showed that the primary phase was Y123.

Samples #4-12 were prepared from the constituent oxides and carbonates. For all of these samples, the powders were mixed by mortar and pestle, pressed into a disk in a uniaxial press at 5.52×10^7 Pa and calcined at 750C for 48 hours and then calcined at 790C for 48 hours. The disk was then reground with mortar and pestle, repressed with a uniaxial press to 5.52×10^7 Pa, pressed isostatically to 3.45×10^8 Pa and sintered at 825C for 100 hours.

Samples #4-7 were prepared from a stoichiometric Y124 powder composition. Sample #4 was sintered in vacuum at 750C for 48 hours, and then in flowing O₂ for 48 hours at 750C, and then held at 800C for 4 days. Sample #5A was mixed as a powder of precursors, pressed into a 1.59 cm disk and put into a furnace in an Al₂O₃ boat in flowing O₂; the temperature was raised in O₂ to 800C and held for 96 hours. Our XRD measurements showed excellent agreement with XRD literature for Y124. This was the first complete synthesis of Y124. At best all preceding samples were a mixture of Y123 and Y124.

For sample #5B, the furnace was heated to 920C and then an O₂ flow was initiated. The sample was then pulled from the cool end into the hot zone, held for 4 minutes at 920C, removed from the hot zone and cooled to 750C, held at 750C for one minute. The sample was then pulled to the cool zone, the furnace was lowered to 450C, the sample was held at 450C for 2 hours in O₂ and then pulled to the cool zone and removed. XRD showed mostly Y123 with the possibility of some Y₂BaCuO₂ and CuO; the extra phases were difficult to detect because of the Y123 reflections.

Sample #6A was treated the same as Sample #5A except that it was heated to 825C for 100 hours. Attempts to measure RF surface resistivity were unsuccessful. XRD gave Y124 as the compound. Sample #6B had XRD of Y124 with an RF resistivity resonance T_c of 74.0K.

Sample #6C: precursors were mixed in a boron carbide mortar and made into two 1.59 cm disks. The disks were put into an Al₂O₃ boat in O₂, heated 825C for 100 hours. AC susceptibility measurements of T_c gave an average reading of $T_c=79.2$ K. Sample #7, powder mixed in mortar, gave AC susceptibility T_c of 80K.

Sample #8 is Ca substituted Y124, Y_{1-z}Ca_zBa₂Cu₄O₈, z = .025. Loose powder was pressed into Al₂O₃ crucible and calcined to 790C in vacuum; held for 48 hours then slowly cooled to 100C. The powder was reground and was axially pressed into a 1.59 cm disk, and was sintered 100 hours at 825C in O₂; subsequently it was slowly cooled to room temperature and removed. An AC susceptibility T_c of 73.5K was obtained.

For Sample #9A, Ca substituted, z = .05, x = 0, the AC susceptibility gave T_c average = 69.45K width 3.1K. A calcining of Sample #9A was done at 770C in vacuum and a sintering was done at 825C for 120 hours. A laser ablated thin film from a Y124 target, No AT-9, was deposited at 150 mTorr pressure of O₂. The film was shiny and exhibited a Y123 + Cu O in XRD. The film was placed in an alumina boat in a quartz tube and was heated to 800C in O₂. Subsequently the film was held for 48 hours at 800C and cooled to 300C in O₂, then held over the weekend at 300C, then removed. The shiny film dulled somewhat. The film had retreated from the edges. (The left hand rectangle represents the film out to the edges; the right hand rectangles represent the film in the center pulled away from the edges.)

Sample #9B; Y124 (.05 Ca for Y), underwent calcining in vacuum at 770C for 70 hours after which the sample was reground and made into disks 1.59 cm; then sintered at 825C in O₂ for 120 hours.

Sample #9C is Y_{1-z}Ca_zBa₂Cu₄O₈; z = .05, x = 0. The weighed out precursors of Sample #9C were mixed by hand in a boron carbide mortar and pestle (t = 1/2 hour). Sample #9C was packed into an alumina boat and was slowly raised to 775C under vacuum; held for 60 hours; cooled slowly in O₂ till room temperature was reached and removed. The powder was reground and pressed into 1.59 cm disks and sintered at 825C for 120 hours with O₂. T_c by AC susceptibility was 75K.

PREPARATION OF THIN FILM Y124 BY LASER ABLATION

Preparation of Y124 laser ablation target: 2BaF₂ + 1/2 Y₂O₃ + 4 CuO were weighed out.

Sample #10, Y124 (.025 Ca for Y) had the lowest surface resistivity to date.

Sample #11: After the usual mixing of the constituents the powder was pressed at 3.45 x 10⁷ Pa in an axial die into 3.18 cm disk; this was followed by isostatic pressing at 3.45 x 10⁸ Pa. The disk was heated to 800C in 6 hours, then was held at 800C for 12 hours and was cooled for 10 hours to room temperature.

Sample #12, YBa₂Cu_{3.95}Li_{.05}O₈ was prepared in the usual way by mixing the powder by hand with boron carbide mortar and pestle. XRD gave Y124 with contraction of all the lattice parameters. T_c average as determined by AC susceptibility was 68.9K. T_c average as determined by RF surface resistivity measurements was 59.8K width 5.8. Sample #12 was used as a target for laser ablation of Y124 on a MgO substrate being held at 730C during deposition and a pressure of 250 mTorr applied during ablation. The resulting film was brown, not shiny, and exhibited a very large resistance. The film was annealed for 2 hours at 800C in O₂ flow and slowly cooled to room temperature in O₂. This pulsed laser ablated film then was examined by XRD and showed peaks of MgO (200) and several small peaks, some of which could be read as beginnings of Y123 or Y124.

CONCLUSIONS

Substitution of Ca for Y results in an increase in T_c. Y_{1-z}Ca_zBa₂Cu₄O₈ with z = .05 gave the maximum rise in T_c = 3K from 82-85K followed by a reduction in T_c with increasing Ca. Li substituted for Cu causes enhanced sintering and increases the mechanical strength of Y_{1-z}Ca_zBa₂Cu_{4-x}Li_xO₈.

Ca substituted 124 yields a low surface resistance of about 120 mΩ at 34K and 35 GHz.

Thin films of Y_{1-z}Ca_zBa₂Cu_{4-x}Li_xO₈ have two principal advantages in microwave applications. They do not undergo a phase transition at 700C as YBa₂Cu₃O₇ does and consequently show no twinning and stress defects. Secondly, Y_{1-z}Ca_zBa₂Cu₄O₈ is stable with respect to oxygen loss up to the decomposition temperature of 850C. Attempts to prepare thin films of Y124 on MgO substrata were unsuccessful. Perhaps a method of silk screening would afford a film of Y124.

We have been making thin films of Y123 routinely by laser ablation. Fabrication of Y123 targets by standard solid state ceramic technology is straightforward. We have prepared ceramic targets of Y124. Attempts to prepare thin films of Y124 from these targets have not been successful primarily because an oxygen pressure of 150 mTorr to 250 mTorr at 730C is required for pulsed laser ablation.

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